γ–PHASE IN WC–Co CEMENTED CARBIDES①

Liu, Shourong
Tianjin Institute of Hard Alloy, Tianjin 300222, China

ABSTRACT

The allotropic transformation process of the γ–phase in WC–Co cemented carbides has been explored. The concepts of γ–grain and the γ–domain have been proposed forward: The γ–domain is the residual *FCC*–type β–Co grain that failed to transform when cooling alloy sample and γ–base is the *HCP*–type α–Co transformed mainly by means of diffusion, the outline of the γ–grain is consistent with the newly fromed β–Co grain formed at high temperature. The quantity and distribution of γ–grain domain are related to the cooling rate after sintering and influence the alloys properties.

Key words: WC–Co cemented carbides γ–grain γ–domain

1 INTRODUCTION

May reported studies have shown that the γ–phase of WC–Co alloys is polycrystalline[1–4]. Due to the complexity of the allotropic transformation in Co–based solid solution, the studies of factors affecting structural composition of the γ–phase in WC–Co alloys at room temperature have been insufficient, especially the concept of γ–domain[5–6]. The author has made further experimental studies on the basis of the former work[7], has put forward the different concepts of γ–grain and γ–domain in WC–Co cemented carbides and has discussed the allotropic transformation of the γ–phase in WC–Co alloys.

2 EXPERIMENTS AND RESULT

2.1 *Experimental*

WC–Co alloy samples possessing different WC grain size and Co contents made on the basis of conventional powder metallurgy engineering by means of liquid–phase sintering. The γ–domain has been revealed with LSR–10 chemical etchant or electrolytic method. The γ–grains were displayed by SEM back-scattered electron imaging. The relative composition of α–Co to β–Co in the γ–phase was analyzed by the D / MAX–RC X–ray diffractometer and compared with metallographic results. The chemical composition in every zone of γ–domain and γ–grains was analyzed with EDAX. The alloy properties, such as bending Strength σ; hardness, HV; specific saturation magnetization, $4\pi\sigma$; and coercitive force H_c were measured by conventional methods.

The changes in the γ–domain resulting from variation in the cooling rate, working deformation and stress was examined by means of altering the cooling rate after sintering, quenching, spark discharge wire cutting and different metallographic preparation techniques.

2.2 *Results*

2.2.1 The Morphology of γ–phase in WC–Co Cemented Carbides

The γ–grain morphology usually remains

---

①Manuscript received June 10, 1992

clear at the sintering surface of WC–Co alloy samples (Fig.1(a)). The γ–boundaries at the polished surface of samples could hardly be revealed by chemical etching but could be seen by SEM back-scattered electron imaging (Fig.1b). The γ–phase in WC–Co alloy usually consists of equiaxial polycrystals which are close in size (about 0.4~ 1.2 mm) and are separated from each other along boundaries. The γ–grain features on the sample surface similar to that in sample interior.

The γ–domains on polished sample surfaces can be repeatedly revealed by chemical etching. OM high magnification observation has shown that the pictrure constract of the γ–domain, with its base, is based on differences of corrosion resistance to the chemical etchant (Fig.2(a)). There is universally a γ–domain in WC–Co alloys with different cobalt contents even in pure cobalt. The γ–domain in sintered state WC–Co alloys distributes nonuniformly in the base in the form of equiaxial or approximately equiaxial isolated islands, and usually through the pores, holes or impurities at the core eutectic graphite can penetrate the γ–domain. The γ–domian size seems independent of Co content in samples and is highly varied scattered (10~ 700 μm), as shown in Fig.2(b), (c).

The γ–domains in the surface layer of WC–Co alloy distribute with some regularity (Fig.3(a)). The γ–domain in quick cooled quasi-eutectic WC–Co alloys about 66.67 wt.–% Co is dendritic (Fig.3(b)). In the surface layer of sintered pure cobalt samples, the γ–domains are connected each other as the bright ferrite layer in decarburized Fe–C alloy sample surface.

2. 2. 2 The Structural and Compositional Features of γ–phase in WC–Co Alloys

It is evident from Fig.3 that the γ–domain can be dendritic, so it is a single–phase crystal[8]. The H_m value is slightly differential in the γ–domain image and also by back-scattered electron images. Difference in wolfram content in exterior and inner areas of the γ–domain haven't been detected by EDAX, though the solid solubility in β–Co is greater than that in α–Co. Since the γ–domain in pure cobalt samples can be clearly revealed by chemical etching (Fig.2(c)). So the difference in corrosion resistance between the γ–domain and the γ–base doesn't lie in their compositions but in their structures. The X–ray diffraction phase analysis shows that the γ–phase of WC–Co alloys, usually consists of two different allotropics, α–Co and β–Co not only on the surface but also in the interior of sintered WC–

Fig. 1 γ–grains of WC–20Co alloy

(a)—on the sample surface, OM(× 25); (b)—on the polished surface, SEM(× 21)

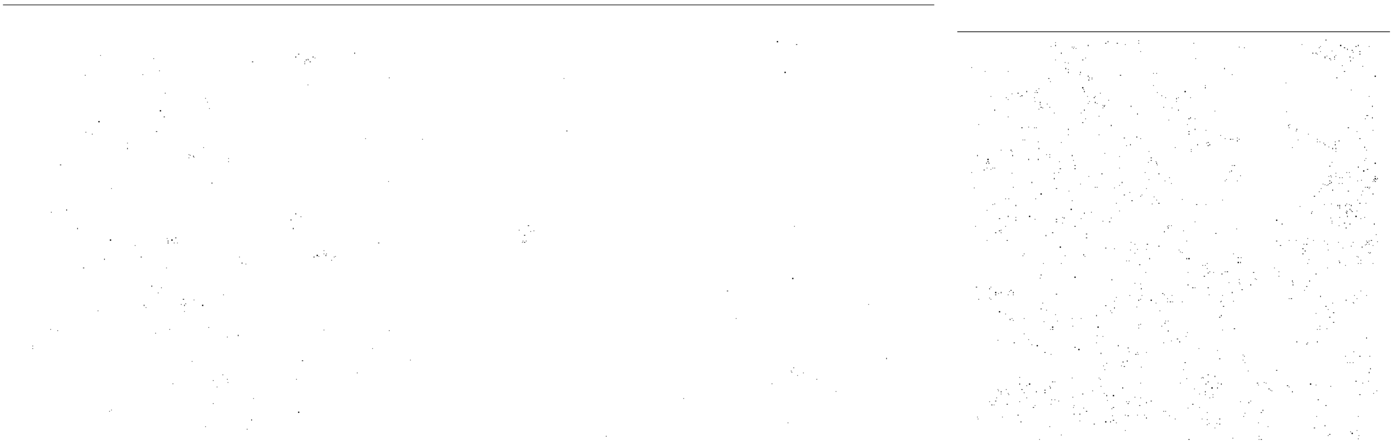

Fig. 2 γ–domain in WC–Co alloy

(a)—WC–15 Co alloy, OM(×300); (b)—WC–20 Co alloy, OM(×25); (c)—sintered pure cobalt, OM(×25)

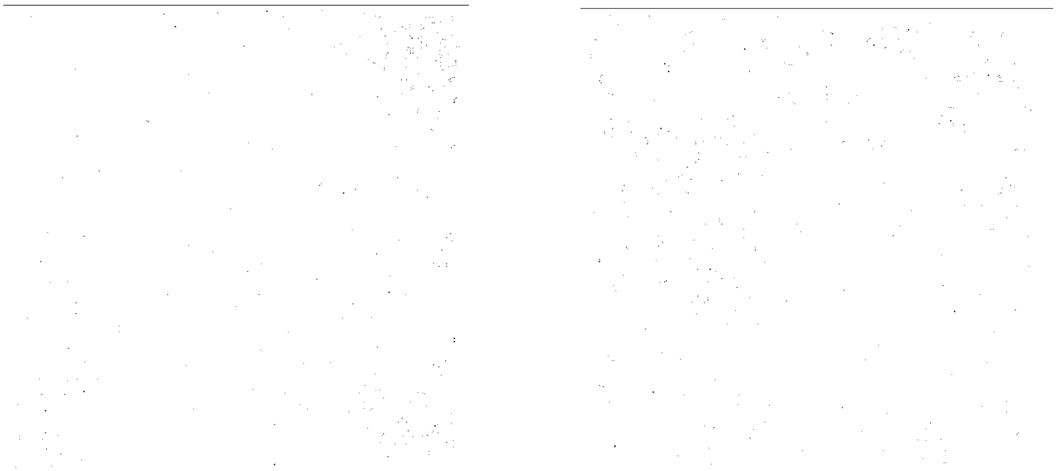

Fig. 3 γ–domain distribution in WC–Co alloys

(a)—on the surface layer of WC–15 Co alloy, OM(×25);

(b)—the dendritic γ–domains of quasi-eutectic WC–Co alloy, OM(×25)

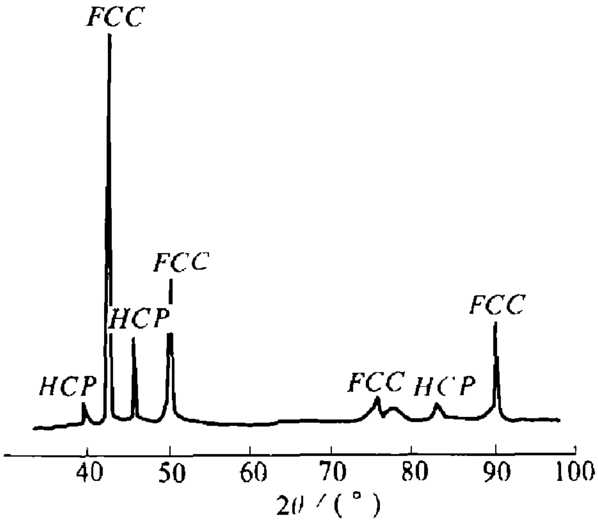

Fig. 4 X–ray diffraction pattern of γ–phase on sample surface layer in WC–20Co alloy

Co samples at room temperature, as shown in Fig.4.

The relative compositions of the above γ–phase allotropies in WC–Co alloys with different Co contents, determined by means of X–ray phase analysis is consistent with the metallographic results. For the above reasons, the γ–domain is *FCC*–type β–Co and the γ–base *HCP*–type α–Co.

But the SEM back-scattered electron image can display the γ–grains on the uncorroded polished sample surface (Fig.1(b)). The EDAX result showed too that the W content in the interior of the γ–grain is less than that in the grain boundaries.

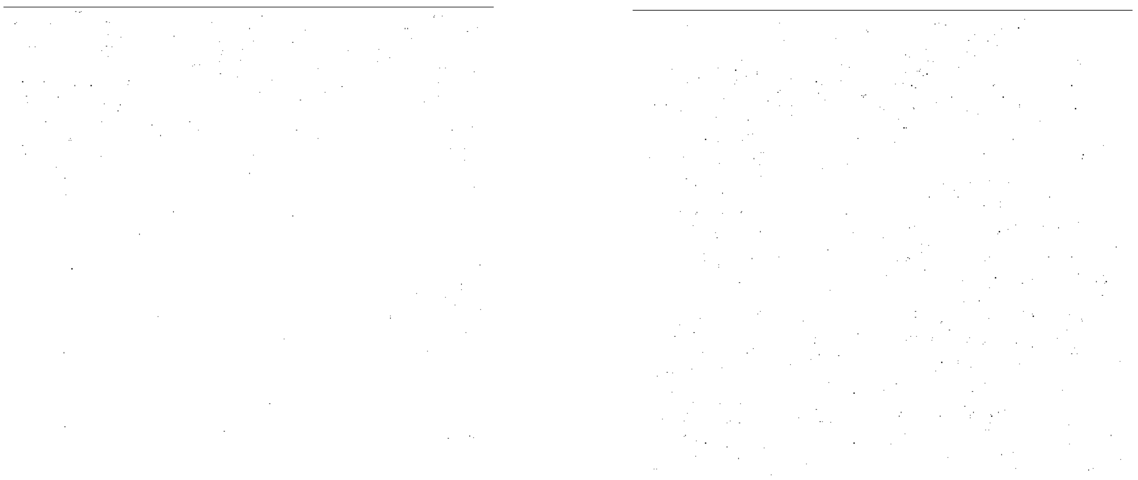

Fig. 5 Effect of wire cutting machining on the γ–domain in WC–20 Co alloy

(a)—sintered; (b)—wire cutting machined

2. 2. 3 The Factors Affecting the γ–domain in WC–Co Alloy

Increasing the cooling rate after sintering and quenching can result in a fine and well distributed γ–domain and an increase in its relative content in alloy samples[7]. Molybdenun wire cutting machining can increase the relative content and evidently decrease the size of γ–domain at the heat influenced layer (Fig.5(a), (b)). The distribution pattern of the γ–domain in the sintered surface of WC–Co alloys represents the surface temperature field formed at the beginning to solidify γ–phase (Fig.3a). Similar regularity in the distrilution of the γ–domain in the interiors of sample hasn't been found.

There are coarse grains and a greater relative amount of γ–domain in fine WC grain alloy than in coarse grain alloys formed with the same Co content and under the same condition. For example, the γ–domain sizes are respectively 0.1 ~0.6 mm and 0.01~0.18 mm in fine WC–20 Co alloy and in coarse WC–20 Co alloy.

The relative content of β–Co in the γ–phase and the γ–domain in alloy samples analyzed respectively by X–ray diffraction analysis and metallographic examination consistently decreased when altering the metallographic preparation to form different degrees of deformation degree and residual stress. However the morphology of the γ–grain in samples didn't changed. But after polishing the WC–80 Co alloy sample by means of the technique explained in Ref.[9], X–ray diffraction of β–Co and quantative metallographic examination of the γ–domain showed that the relative amount of β–Co in the γ–phase and γ–domain in alloy sample approached 100%. It is showed that the degree of deformation resulting from the preparation process is extremely small and the outlines of the γ–grain and γ–domain are identical with each other (Fig.6).

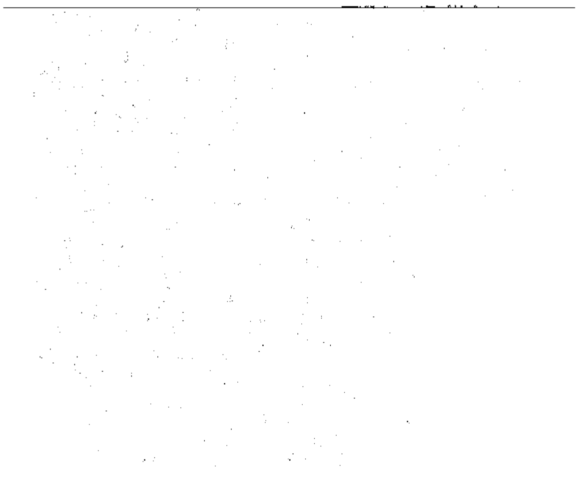

Fig. 6 γ–domains in WC–80 Co alloy

Analyzing the WC–20 Co sample in which surface there was 90% γ–Co(by X–ray analysis), after grinding away 0.2 mm thickness showed that the γ–grains remained the same, but the amount of γ–domain decreased to 80% which indicates, compared to the surface layer, the relative amounts of γ–domain at the surface layer and in interior of the sample were quite different.

2.2.4 Relationship of the γ–domain to the Properties of WC–Co Alloys

Quenching WC–Co alloys samples with different Co content by holding them for 30 min at 1 250 ℃ in H_2 can make the γ–domain fined, well-distributed and raised, its relative amount increaced. The raised amount of bending strength are respectively: WC–6Co, 4.2%; WC–10Co, 5.0%; WC–20Co, 9.0% and WC–20C Co, 10.0%. The Vickers indentation crack length for WC–20Co alloy with 30 kg load decreased from 67 μm to 45 μm, i.e. the toughness improved, and correspondingly the specific saturation magnetization, $4\pi\sigma$, decreased while the magnetic coercivity force H_c raised.

3 DISCUSSION

The literature[10,11]shows that, the M_s transformation temperature. of *FCC*—→*HCP* in pure cobalt is 700 K. Owing to the solution of W in the γ–phase and the mechanicals restraint role of WC grains, a rigid skeleton increases the stability of the β–Co and reduces the non-diffusible M_s transformation temperature to room temperature. Therefore, the γ–phase of WC–Co alloys is β–Co at room temperature and the small amount of α–Co in it results from plastic deformation or shear stress induction at room temperature.[1].

But past work[7,8,12]showed that the γ–phase of pure cobalt and WC–Co alloys was usually a mixture of α–Co and β–Co. There was a little α–Co, even also in the sintered surface layer of the sample. Also there should be more influence on deformation or shear stress and less mechanical restraint by a rigid WC skeleton on the γ–phase in high cobalt content WC–80 Co alloy than in low cobalt content WC–20Co alloy when prepared metallographically, but there was 100% high β–Co at the polished surface of WC–80Co sample. This means that the existence of α–Co in WC–Co alloys at room temperture resulted mainly from the phase transformation when cooling the samples beyond the M_S temperture, even if considering the influence deformation of stress.

Consequently, the *FCC*—→*HCP* transformation of a cooling alloy sample after sintering may be thought to proceed by means of diffusible and nondiffusible martensite type and to follow nucleating and growing regularities. Alloy samples usually stayed for a long time in the low-temperature zone and the cooling end of the sintering furnace. The cooling rate is usually lower after sintering furnace above the M_s temperature. Therefore the transformation mentioned above is mainly diffusible. Because this process proceeds slowly, the γ–phase is mainly β–Co at room temperature.

When cooling to the liquidus line, the β–Co nuclei form from the liquid γ–phase and the nuclear formation rate is restricted by the degree of surpercooling degree. Once growing β–Co grains contact each other, the β–Co polycrystal, i.e. the newborn β–Co grains, forms. The formation of Solid β–Co grains results in local volume contraction, neighbouring liquid phase filling up and a pushing off of the primary WC grains to the newborn γ–boundaries.

When cooling to about 1 000 k[12], the α–Co crystal nuclei, governed mainly by diffusion, form at the newly formed γ–boundaries, i.e. β–Co boundaries, and grow towards the interior of the γ–grain as the temperature falls. The transformed portion is the γ–base (α–Co) and the remainder is the residual β–Co grains i.e. γ–domains at room temperature. The composition difference between the γ–domain and γ–base lies only in the solubility of W in them, which was barely distinguished with EDAX. In the cooling of solid WC–Co alloy, the newly formed γ–grain morphology and the WC grains distribution can remain mainly unchanged to room temperature, but the size and the shape of the γ–domains can changed in various degrees, although their size is less than that of a γ–grain. In view of the expectation that the dendrite grain should disappear after allotropic transformation[13], the existence of the dendrite grains (see in Fig.3b) shows that the γ–domain is just residual *FCC*–type β–Co. Furthermore, regardless on the basis of the noncrystalline bonded boundary theory or the transitional lattice boundary theory, large zone (more than 100 times the size of cobalt atom interval) and homogeneous composition and structure of the γ–base show that the γ–base is an independent phase but not the boundary.

Because the undulations of temperature and composition are not identical at different positions in an alloy sample, the *FCC*—*HCP* transformation of γ–phase is non-uniform. Therefore, the newly formed β–Co grains (γ–grains) can be completely or partially transformed to α–Co, Therefore the γ–domain is non-uniform in distribution and variable in size at room temperature. The energy of the β–Co grains lying in defects such as pores holes, etc., is low, so they easily remain unchanged (Fig.2(b)).

The two forms of *FCC*⟶*HCP* transformation in the γ–phase are not strictly separated. The non–diffusible (M_s) transformation intensifies as the cooling rate rises, but the diffusion is still principally above the M_s temperature. Therefore, the higher the cooling rate, the less the amount of α–Co transformed and the greater the amount of γ–domain. The greater γ–domain in the sintered surface than in the interior of alloy samples and the connected γ–domains at the surface layer in pure Co samples resulted from the higher cooling rates at surfaces than in the interiors of Sintered samples.

As the temperature rises before quenching, the β–Co nuclei first form at γ–boundaries, which have high W content and grow towards the grain interior to connect the γ–domain and the α–Co turns completely into β–Co beyond 1 000 K at which point the γ–grain size and WC grain distribution basically remain unchanged. Extremely rapid supercooling rate in subsequent cooling brings about the high nuclear formation rate of α–Co and resulting in a greater amount and more homogeneous distribution of γ–domain at room temperature.

When wire cutting, the γ–phase at the machined surface melts. The extreme supercooling rate resulted from the deionized water which leads to a high nuclear formation rate of β–Co. Therefore, the newborn γ–grains are fine. When solid alloy subsequently cools, the *FCC*⟶*HCP* transformation of the γ–phase takes place. The α–Co nuclei form preferentially at γ–boundaries (energy factor). Because of the great amount of γ–grain boundaries and extreme super cooling rate, the resulting α–Co is scattering in distribution and less in quantity. Correspondingly, there is finer size, more even distribution and a greater amount of γ–domain in the machined surface layer than in the sample interior.

For the same Co content, the lower composition undulation in fine WC grain alloy than in coarse grain alloys when liquid γ–phase begins to solid leads to lower nuclear formation rates of β–Co. In addition the coarser newly formed γ–grains and lowed amount of γ–boundary lead to coarse γ–domains at room temperature.

Due to the more slip systems and greater solid solubility of W in β–Co than in α–Co, β–Co was better plasticity and toughness. Hence, any processes favouring increasing the amount of γ–domain and homogenizing its distribution (for example quenching) would lead to improve strength and toughness of WC–Co alloys. The effect of γ–phase structure on alloy magnetism is less than that of its content. Therefore, the increase the increment of W solid solubility in γ–phase by quenching would necessarily lower the $4\pi\sigma$ and raise the H_c of WC–Co alloy, though the increase of the γ–domain would have the opposite effect.

4 CONCLUSIONS

(1) The γ–domain in WC–Co cemented carbides consists of the residual *FCC*–type β–Co grains that fail in transformation when the alloy is cooled after sintering. The γ–base is the *HCP*–type α–Co transformed mainly by means of diffusion, the outline of the γ–grains is consistent with the newly formed β–Co grains formed at high temperature. Under the existence of two types of γ–solid solution at room temperature, the γ–domain isn't identical with the γ–grain but is a part of the γ–grain i.e. the residual *FCC* β–Co;

(2) The γ–domain and the γ–grain in WC–Co alloy can be respectively revealed by LSR–10 etchant and displayed with SEM back-scattered images. The revelation of a γ–domain provides a simple visual method for identifying β–Co in WC–Co alloys;

(3) The γ–domain and the γ–grain in WC–Co alloys are all usually equiaxial or approximately equiaxial. Their sizes are respectively 10 ~ 70 μm and 0.4 ~ 1.2 mm. The γ–domain usually distributed in the γ–base in the form of "isolated island", and its size and distribution are affected by the cooling rate after sintering and related to the newly formed γ–grain size;

(4) The proportional volume and distribution features of the γ–domain can evidently affect the strength and toughness of WC–Co alloy.

REFERENCES

1 Virwanhai, R K. Metallography, 1979, 12: 333.
2 Willbrand, J *et al.* Journal of Powder Metallurgy, 1972, 8(2): 89–93.
3 Almond, E A *et al.* In: proceedings of 10th Plansee Seminar, Metallwerk Plansee, Reutte, Austria. 1981, 1: 659.
4 Liu, Shourong. The Chinese J of Transactions of Metal Heat Treatment, 1991, 12(4): 48(in Chinese).
5 Lingmushou, *et al.* Powder and Powder Metallurgy, 1973, 19 (8): 346–353 (in Japanese).
6 Suzuki, H *et al.* Planseeber Pulverment, 1979, 27: 215(in German).
7 Liu, Shourong. The Chinese J of Transactions of Metal Heat Treatment. 1988, 9(2): 32–34(in chinese).
8 Wumansji, Y S *et al.* The Chinese Translation of the Basis of Metallic Physics, 1958, 318.
9 Liu, Shourong. Physical Testing and Chemical Analysis (physical Testing). 1988, 24(1): 42(in Chinese).
10 Exner, H E. Science of Hard Materials Viswanadham, R K *et al*), (Eds) New york: Plenum press, 1983, 239.
11 Suzuki, H *et al.* J. Japan. Inst Metals, 1968, 32: 993.
12 Giamei, A F *et al.* Cobalt, 1968, 40: 140.
13 University of Science and Technology Beijing *et al.* Metallurgy and Heat Treatment. Beijing: China Industrial Press, 1961, 38 (in Chinese).